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(54) Process for the preparation of hydrotreating catalysts form hydrogels.

(57) Process for preparing highly active hydrotreating catalysts prepared by incorporating a metal selected from the group consisting of molybdenum, tungsten and mixtures thereof, cobalt or nickel (with a stabilizing amount of phosphorus) into an alumina hydrogel support. The final calcined catalysts have surface areas greater than 300 m^2/g, crush strengths greater than 80 N and more than 80% of their pore volume in pores having diameters less than 7 nm.

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PROCESS FOR THE PREPARATION OF HYDROTREATING CATALYSTS FROM HYDROGELS

The present invention relates to a process for preparing highly active alumina hydrogel-derived catalysts.

In the catalytic processing of petroleum feedstocks, it is often desirable to alter the pore structure of the catalyst in order to accommodate different types of feeds. For example, when processing feedstocks of high metals content, the metals tend to deposit rapidly on the catalyst surface and plug the pores of conventional hydroprocessing catalysts, resulting in a loss of catalytic activity for sulphur and nitrogen removal. To facilitate the diffusion of large components into and out of the catalyst and to prevent surface deposits of coke and metals, large pore diameters are required. On the other hand, when processing feedstocks with no metals or with low metals contents, it may be technically and economically desirable to use narrow-pore catalysts. For purposes of denitrification, narrow-pore catalysts normally have higher activities and longer lives than catalysts containing large pores which tend to deactivate quickly.

The present invention relates to a process for preparing highly active hydrotreating catalysts having surface areas above 300 m^2/g and at least 80% of the pore diameters less than 7 nm which process comprises

(a) precipitating an aqueous solution of one or more aluminium salt(s) by adjusting the pH of said solution to a range between 5.5 and 10.0 at a temperature in the range between 20°C and 90°C, thereby forming a precipitate,

(b) ageing the precipitate at a temperature ranging from 20°C to 90°C for at least 15 minutes at a pH ranging from 8.0 to 12.0,

(c) washing the precipitate,

(d) mixing the precipitate with dry, water-soluble salts of a heavy metal selected from the group consisting of molybdenum, tungsten and mixtures thereof and either of cobalt or of nickel and a phosphorus-containing compound in an amount of from 0.2 to 1.5 moles of phosphorus per mole of heavy metal, at a pH in the range between 4.0 and 8.0 and a temperature in the range between 25°C and 100°C to yield a final catalyst having from 1%w to 5%w of cobalt or 5%w nickel and from 8%w to 32%w heavy metal,

(e) extruding the product of step (d), and

(f) drying and calcining the product of step (e) at a temperature ranging from 300°C to 900°C.

It has been found that hydrogel-derived catalysts can be prepared using the hydrogel as a solvent in the reaction of the hydrogel with metal salts. One of the benefits of adding no additional water when the metal salts are added to the hydrogel is that less metal is lost to the effluent during washing. In addition, catalysts prepared using a hydrogel route have activities equal to or better than catalysts prepared by conventional impregnation techniques when compared on a volumetric basis while having densities significantly lower than conventionally prepared catalysts. Two of the major advantages of the hydrogel route are higher metals utilization and lower costs of catalyst manufacture. The catalysts prepared according to the process according to the present invention have high surface areas, greater than 300 m^2/g; high flat plate crush strengths, greater than 80 N; and substantial portions, greater than 80%, of their pores with diameters less than 7 nm. These catalysts are particularly useful for hydrotreating applications.

In the process according to the present invention highly active hydrotreating catalysts are suitably prepared by incorporating a heavy metal selected from the group consisting of molybdenum, tungsten and mixtures thereof, cobalt or nickel and phosphorus-containing compounds into an alumina hydrogel-derived support prepared by titrating an aqueous solution of an acid aluminium compound and an aqueous solution of a basic aluminium compound.

The alumina hydrogel can thus be prepared by titrating an aqueous solution of one or more aluminium salt(s) with an appropriate acidic or basic material or solution to cause precipitation of the alumina gel. Those skilled in the art will recognize that the alumina gel can be prepared in a number of ways, e.g. by titrating an acidic aluminium salt such as, for example, aluminium sulphate, aluminium nitrate or aluminium chloride in aqueous solution with a basic precipitating medium such as, for example, sodium hydroxide or ammonium hydroxide or by titrating an alkali metal aluminate such as, for example, sodium aluminate or potassium aluminate, in aqueous solution with an acidic precipitating medium such as, for example, hydrochloric acid or nitric acid. Those skilled in the art will recognize that the adjustment of the pH of an aluminium-containing solution to between 5.5 and 10.0 will result in precipitation of the aluminium as aluminium hydroxide or hydrated aluminium oxide.

In a preferred embodiment, the alumina hydrogel is prepared by titrating an aqueous solution of an alkali metal aluminate and an aqueous solution of an acid aluminium salt to cause precipitation of the alumina gel. Suitable acidic aluminium salts include aluminium sulphate, aluminium nitrate and aluminium chloride. A preferred species is aluminium chloride. Suitable alkali metal aluminates are sodium aluminate and potassium aluminate. The precipitation can be carried out by adding an aqueous solution of the basic aluminium species to an aqueous solution of the acidic aluminium species or the procedure can be reversed by adding an aqueous solution of the acidic aluminium species to an aqueous solution of the basic aluminium species (referred to as "sequential precipitation"). Preferably, the precipitation in the process according to the present invention is carried out by simultaneously adding the acid aluminium species and the basic aluminium species to cause precipitation of the hydrogel (referred to as "simultaneous precipitation").

The temperature and pH of the precipitation are important variables in the preparation of the aluminas into which dry metal salts can be incorporated to form hydrotreating catalysts with desirable physical qualities. Changes in precipitation temperatures and pHs result in changes in porosities. In the process according to the present invention, a precipitation temperature typically ranges from 20°C to 90°C, and preferably from 50°C to 85°C, and a precipitation pH typically ranges between 5.5 and 10.0, preferably between 5.5 and 8.0, and more preferably between 6.0 and 7.5. The length of time required for the precipitation step is not critical. However, the maximum rate of addition of the acid aluminium species and the basic aluminium species is fixed by the rate at which the two streams can be mixed and the pH and temperature of the system can be effectively controlled.

After precipitation has taken place, the pH of the slurry is adjusted by addition of a basic aluminate solution to fall in the range from 8.0 to 12.0, preferably 9.0 to 11.0, most preferably 9.5 to 10.5, and aged at a temperature in the range from 20°C to 90°C, preferably 50°C to 85°C for at least 15 minutes. An upper limit on the length of time for ageing is not critical and is normally determined by economical considerations. Ageing times will typically range from 0.1 to 10 hours, preferably from 0.25 to 5 hours, and more preferably from 0.25 to 1 hour. In general, aluminas with acceptable properties are produced by holding the ageing temperature substantially equal to the precipitation temperature.

After ageing, the slurry is washed and filtered in routine fashion to remove substantially all the salts formed during the precipitation of the hydrogel which can be removed by washing. The preferred solvent for washing is water although other solvents such as lower alkanols may be utilized.

After washing, the precipitate is mixed with dry, water-soluble salts of a heavy metal selected from the group consisting of molybdenum, tungsten and mixtures thereof and cobalt or with nickel, and a phosphorus-containing compound an amount of from 0.2 to 1.5 moles of phosphorus per mole of heavy metal. The hydrogel and the salts are mixed until dissolution and adsorption of the metal salts is essentially complete. The metal salts of nickel or cobalt and molybdenum and/or tungsten are added to the hydrogel in amounts sufficient to incorporate into the final calcined catalyst from 1%w to 5%w of cobalt or nickel and from 8%w to 18%w molybdenum or 10%w to 32%w tungsten. When mixtures of molybdenum and tungsten are utilized, the final catalyst normally contains 8%w to 32%w molybdenum and/or tungsten.

Preferably, molybdenum is added to the hydrogel in the form of a dry, water-soluble source of molybdenum such as ammonium heptamolybdate or ammonium dimolybdate. Tungsten is preferably added to the hydrogel as ammonium metatungstate. Nickel is preferably added to the hydrogel in the form of dry, water-soluble nickel nitrate, nickel acetate, nickel formate, nickel sulphate, nickel oxide, nickel phosphate, nickel carbonate, nickel chloride or nickel hydroxide, with nickel nitrate and nickel carbonate being preferred. The phosphorus-containing compound is preferably added directly to the hydrogel as phosphoric acid, a phosphate salt or mixtures thereof. Suitable phosphate salts include alkali metal phosphates, alkali metal hydrogen phosphates, ammonium phosphate and ammonium hydrogen phosphate. Alternatively, the phosphorus-containing compound and the dry nickel salt can be mixed prior to addition to the hydrogel. As used herein, the term "phosphorus-containing compound" is generic and refers to one phosphorus-containing compound as well as more than one phosphorus-containing compound. Cobalt is preferably added to the hydrogel in the form of dry, water-soluble cobalt nitrate, cobalt hydroxide, cobalt acetate, cobalt oxalate or cobalt oxide, with cobalt nitrate being preferred. In a preferred embodiment, a phosphorus-containing compound in an amount of phosphorus in the range from 0.2 to 1.5 moles of phosphorus per mole of molybdenum or tungsten is added directly to the hydrogel.

A preferred method of mixing the dry metal salts of nickel or cobalt and molybdenum and/or tungsten with the hydrogel comprises adding hydrogen peroxide to the mixture in an amount ranging from 0.1 to 1.0 mole of hydrogen peroxide per mole of molybdenum and/or tungsten. Optionally, a suitable amine compound such as monoethanolamine, propanolamine or ethylenediamine may be added to the mixture in order to add in stabilization of the mixture.

The dry metal salts of nickel or cobalt and molybdenum and/or tungsten are typically added to the hydrogel in the form of finely divided particles which are generally 0.15 mm or less in size. While particle size is not critical and larger particles may be utilized, it is economically advantageous to use particles which are 0.15 mm or less in size.

The temperature and pH of the mixing step are both important variables in the preparation of hydrogel-derived catalysts which have acceptable densities and porosities. In general, high temperatures in the mixing step result in lower density catalysts. The pH of the mixing step, however, appears to be critical to the formation of catalysts having the desired properties. Upper limits on the pH of the mixing step will be 9.5, preferably 9.0, more preferably 8.5 and most preferably 8.0. Lower limits on the pH of the mixing step will be 4.0, preferably 5.0 and more preferably 4.5. The mixture of the hydrogel support with the dry metal salts is typically carried out at a pH in the range between 4.0 and 8.0, preferably between 4.0 and 6.0, adjusting to these pH ranges by adding, if necessary, acid or base to the hydrogel and/or the mixture of the dry metals and the hydrogel, and a temperature in the range between 25°C and 100°C, preferably between 25°C and 80°C, until adsorption of the metals salts onto the gel is sufficient to yield a final calcined catalyst having from 1%w to 5%w of cobalt or nickel and from 8%w to 18%w molybdenum or from 10%w to 32%w tungsten. Typically, the times for mixing the hydrogel with the dry metal salts will range from 0.5 to 2 hours.

Following the mixing step, the material obtained may be extruded and then dried and calcined; dried, mulled with addition of water, extruded or pelleted and calcined; or partially dried, extruded or pelleted, dried more completely and calcined. Drying is accomplished by conventional means. It may be carried out by forced draft drying, vacuum drying, air drying or similar means. Drying temperatures are not critical and depend upon the particular means utilized for drying. Drying temperatures will typically range from 50°C to 150°C.

In a preferred embodiment, the material is extruded and then dried. Alternatively, the material may be extruded after drying to the proper loss on ignition (LOI). However, to facilitate extrusion, organic binders and/or lubricants may be added prior to extrusion.

After drying, the material is calcined to produce the finished catalyst. The material may be calcined in any atmosphere, reducing, oxidizing or neutral, although air is preferred. However, if binders and/or lubricants are used the material is heated in an oxygen-containing atmosphere, preferably air, in order to burn out the binders and lubricants. Calcining temperatures will typically range from 300°C to 900°C. Drying, calcining and burn-out may be combined in one or two steps. Most frequently the calcining and/or burn-out steps are combined using an oxygen-containing atmosphere.

Certain other processing steps may be incorporated into the above-described procedure without deviating from the scope and intent of the process according to the present invention. For example, prior to the complete drying of the catalyst, it may be extruded and then dried more completely, followed by calcination.

The final catalysts are found to have surface areas greater than 300 m^2/g, pore volumes ranging from 0.4 to 1.2 ml/g and with at least 80% of their respective pore volumes in pores having diameters less than 7 nm. Crush strengths are generally greater than 80 N. In general, the metals contents of the final catalysts range from 1%w to 5%w, preferably from 2.5%w to 4%w of cobalt or nickel, and from 8%w to 18%w, preferably 10%w to 14%w molybdenum or 10%w to 32%w, preferably 18%w to 26%w tungsten.

The catalysts prepared in accordance with the present invention can be suitably applied to hydrocarbon conversion processes such as catalytic cracking, hydrocracking, hydrotreating, isomerization, hydrogenation, dehydrogenation, oligomerization, alkylation, dealkylation and the like.

The catalysts prepared in accordance with the present invention are most commonly employed in hydrotreating feedstocks ranging in volatilities from naphthas to flashed distillates. Reaction temperatures will typically range from 150 °C to 450 °C, preferably from 260 °C to 415 °C. Reaction pressures are generally within the range of 14 to 175 bar, preferably from 42 to 105 bar. Reactions are normally conducted at liquid hourly space velocities within the range of 0.1 to 10 reciprocal hour.

Multiple uses of these feedstock after treating with the catalysts prepared in accordance with the present invention are possible. Depending on the particular feedstocks treated, suitable uses can include conversion unit feedstocks such as cat cracking, thermal cracking and hydrocracking, or finished products such as gasoline, diesel, airline turbine fuel, furnace oils and solvents.

The process for preparing the catalysts in accordance with the present invention will be further described below by the following Examples which are provided for illustration and which are not to be construed as limiting the invention.

Example 1

Seven hundred and forty grams of reagent grade sodium aluminate were added to 1000 grams of water which was then heated to 60°C in order to effect dissolution of the materials. Five hundred and forty-four grams of aluminium chloride hexahydrate were added to 760 grams of water. Both solutions were cooled to slightly less than 60°C and placed in dropping funnels.

Five thousand grams of water were added to a 10 litre stainless steel bucket equipped with a pH meter, thermometer and stirrer. After the pH was adjusted to 7.0 using the sodium aluminate solution, the two solutions in the dropping funnels were added simultaneously to the well-stirred bucket, maintaining a precipitation pH of 7. A total of 1370 grams of sodium aluminate solution and 761 grams of aluminium chloride solution were used to effect the titration. After these quantities of reagents had been used, the final ageing pH of the solution rose to 10.0. The solution was aged for one hour at 60°C. The resulting material was filtered and washed in two large Buchner funnels with about 50 litres of water. The excess water from the wet filter cake was removed by vacuum. The hydrogel was then divided into two equal portions.

A mixture of 30.32 grams of nickel nitrate as hexahydrate and 30.51 grams of 85% phosphoric acid was then prepared. This mixture, along with 45.24 grams of ammonium heptamolybdate and 16.0 grams of 30% hydrogen peroxide, and 8.20 grams of monoethanolamine were directly added to one portion of the hydrogel at 75-80°C at a pH of 5.5. The resulting mixture was then stirred for two hours. At the end of two hours, the slurry was filtered and excess water from the slurry was removed by vacuum. The wet gel was then extruded using a small, hand-held extruder using a 4 mm cylindrical die, dried overnight at 120°C and calcined in air at 510°C. The properties of the catalyst are listed in Tables I and II.

Example 2

Five hundred and eighty-three grams of reagent grade sodium aluminate were added to 787 grams of water which was then heated to 60°C in order to effect dissolution of the materials. Two hundred and seventy-one grams of aluminium chloride hexahydrate were added to 379 grams of water. Both solutions were cooled to slightly less than 60°C and placed in dropping funnels.

Five thousand grams of water were added to a 10 litre stainless steel bucket equipped with a pH meter, thermometer and stirrer. After the pH was adjusted to 7.0 using the sodium aluminate solution, the two solutions in the dropping funnels were added simultaneously to the well-stirred bucket, maintaining a precipitation pH of 7. All of the reagents were used. After the reagents had been added, the final ageing pH of the solution was adjusted to 10.0 using hydrochloric acid. The solution was aged for one hour at 60°C. The resulting material was filtered and washed in two large Buchner funnels with about 50 litres of water. The excess water from the wet filter cake was removed by vacuum. The hydrogel was then divided into two equal portions.

A mixture of 29.64 grams of cobalt nitrate as hexahydrate and 29.9 grams of 85% phosphoric acid was then prepared. This mixture, along with 47.97 grams of ammonium heptamolybdate, 14.18 grams of 30% hydrogen peroxide, and 8.0 grams of monoethanolamine were directly added to one portion of the hydrogel at 80°C at a pH of 5.5. The resulting mixture was then stirred for two hours. At the end of two hours, the slurry was filtered and excess water from the slurry was removed by vacuum. The wet gel was then extruded using a small, hand-held extruder using a 4 mm cylindrical die, dried overnight at 120°C and calcined in air at 510°C. The properties of the catalyst are listed in Tables I and II.

Example 3

A catalyst was prepared as described in Example 2 except that no phosphoric acid was added in the mixing step. The properties of the catalyst are listed in Tables I and II.

Comparative Experiment A

A catalyst was prepared as described in Example 1 except that the pH in the mixing step was adjusted to 10.0 using ammonium hydroxide. The properties of the catalyst are listed in Tables I and II.

Comparative Experiment B

A catalyst was prepared as described in Example 1 except that the pH in the mixing step was adjusted to 2.0 using hydrochloric acid. The materials prepared in this experiment were unsuitable for testing as the alumina support dissolved when the pH was adjusted to 2.0.

Comparative Experiment C

A catalyst was prepared as described in Example 1 except that no phosphoric acid was added in the mixing step. The properties of the catalyst are listed in Tables I and II.

Comparative Experiment D

A catalyst was prepared using a conventional dry pore volume impregnation technique. A solution suitable for impregnating a gamma alumina carrier was prepared as follows. A first solution was made by adding 19.39 grams of nickel nitrate and 16.18 grams of phosphoric acid to 5 millilitres of water which solution was then heated to 40°C and stirred in order to effect dissolution of the materials. A second solution was prepared by mixing 5.5 millilitres of 30% hydrogen peroxide, 30 millilitres of distilled water and 35.20 grams of ammonium heptamolybdate. The mixture was then heated to 40°C and stirred until all solids were dissolved. When both solutions were at or near ambient temperature, the second solution was slowly added to the first solution while stirring. After cooling and diluting with water to match the total water pore volume of the support, the solution was added to the gamma alumina support in several small portions with intermediate agitations. The impregnated support was further agitated during a period of 5 minutes, dried for 2 hours at 204°C and calcined in air for 2 hours at 482°C. The properties of the catalyst are listed in Tables I and II.

Comparative Experiment E

A catalyst was prepared as described in Example 2 except that the pH in the mixing step was adjusted to 10.0 using ammonium hydroxide. The properties of the catalyst are listed in Tables I and II.

Comparative Experiment F

A catalyst was prepared as described in Example 2 except that the pH in the mixing step was adjusted to 2.0 using hydrochloric acid. The materials prepared in this experiment were unsuitable for testing as the alumina support dissolved when the pH was adjusted to 2.0.

Comparative Experiment G

A catalyst was prepared using a conventional dry pore volume impregnation technique. A solution suitable for impregnating a gamma alumina carrier was prepared as follows. A first solution was made by adding 15.37 grams of cobalt nitrate and 9.67 grams of phosphoric acid to 5 millilitres of water which solution was then heated to 40°C and stirred in order to effect dissolution of the materials. A second solution was prepared by mixing 4.0 millilitres of 30% hydrogen peroxide, 40 millilitres of distilled water and 23.39 grams of ammonium heptamolybdate. The mixture was then heated to 40°C and stirred until all solids were dissolved. When both solutions were at or near ambient temperature, the second solution was slowly added to the first solution while stirring. After cooling and diluting with water to match the total water pore volume of the support, the solution was added to the gamma alumina support in several small portions with intermediate agitations. The impregnated support was further agitated during a period of 5 minutes, dried for 2 hours at 204 °C and calcined in air for 2 hours at 482 °C. The properties of the catalyst are listed in Tables I and II.

Catalyst Testing

Catalyst samples were used to hydrotreat a catalytically-cracked heavy gas oil (CCHGO) in a trickle-flow reactor. Ten ml of the appropriate extruded catalyst were crushed and sieved to 0.3-1 mm (16-45 mesh), diluted with silicon carbide, and loaded into a typical trickle-flow reactor tube. The catalyst was presulphided with a 5% H_2S/H_2 (v/v) gas mixture at 371 °C for 2 hours prior to testing. A CCHGO was passed over the catalyst at 343°C and a partial hydrogen pressure of 56 bar with a H_2/oil ratio equal to 4.0. Measured rate constants include hydrogenation, denitrification and desulphurization and are reported relative to the impregnated catalysts (Comparative Experiment D for nickel-containing catalysts and Comparative Experiment G for cobalt-containing catalysts). Specific catalyst performance characteristics are presented in Table III.

TABLE I

Catalyst Properties

	EXAMPLE 1	EXAMPLE 2	EXAMPLE 3	COMPARATIVE EXPERIMENT A	COMPARATIVE EXPERIMENT C	COMPARATIVE EXPERIMENT D	COMPARATIVE EXPERIMENT E	COMPARATIVE EXPERIMENT G
Ageing pH[a)]	10.0	10.0	10.0	10.0	10.0	-	10.0	-
Density g/ml[b)]	0.66	0.67	0.75	0.91	0.85	0.86	0.71	0.77
Reslurry pH[c)]	5.5	5.5	5.5	10.0	5.5	-	10.0	-
N_2 Surface Area m^2/g[d)]	350	366	399	268	429	186	335	190
N_2 Pore Volume ml/g[e)]	0.58	0.42	0.59	0.45	0.42	-	0.53	-
Flat Plate Crush Strength N[f)]	32.0	15.0	19.0	25.0	25.0	17.5	19.0	18.0
%wt. Nickel[g)]	3.3	2.9	2.7	2.3	2.9	2.7	2.6	2.4
%wt. Molybdenum[h)]	10.8	11.6	10.0	6.2	11.6	13.2	4.2	9.8
%wt. Phosphorus[i)]	4.0	4.2	0.0	5.0	0.0	3.0	3.7	2.0

TABLE II

Catalyst Pore Size Distributions

Hg Pore[j] Size Dist.	EXAMPLE 1	EXAMPLE 2	EXAMPLE 3	COMPARATIVE EXPERIMENT A	COMPARATIVE EXPERIMENT C	COMPARATIVE EXPERIMENT D	COMPARATIVE EXPERIMENT E	COMPARATIVE EXPERIMENT F
< 5 nm	23.9	31.8	24.1	59.7	91.1	1.7	52.4	2.9
5 - 7 nm	64.5	60.1	67.4	30.8	2.9	15.3	39.0	14.9
7 - 10 nm	4.7	2.6	2.9	2.7	1.7	29.3	2.5	40.1
10 - 15 nm	3.1	2.0	2.1	2.5	1.9	40.3	2.2	35.9
15 - 35 nm	3.1	2.0	2.1	2.3	1.5	5.1	2.4	4.1
> 35 nm	0.7	1.5	1.4	2.0	0.8	8.4	1.5	2.0

a) Measured using an Orion 231 pH meter and Orion electrodes.

b) 209 ml volume fully settled in a graduated cup and weighed.

c) Measured using an Orion 231 pH meter and Orion electrodes.

d) BET, by nitrogen adsorption/desorption, Micromeritics Digisorb 2500 Instrument.

e) By nitrogen adsorption, Micromeritics Digisorb 2500 Instrument.

f) Flat plate, single pellet, extrudate approximately 5 mm in length.

g) Weight percent determined by neutron activation analysis or atomic absorption spectroscopy.

h) Weight percent determined by neutron activation analysis or atomic absorption spectroscopy.

i) Weight percent determined by neutron activation analysis or atomic absorption spectroscopy.

j) Determined by mercury intrusion, to 4136 bar using a Micromeritics Autopore 9210, using a 130° contact angle and 0.473 N/m surface tension of mercury. Numbers listed are percent pore volume.

TABLE III

Specific Catalyst Performance

	CCHGO (VOLUMETRIC)		
	H	N	S
Example 1	1.34	0.95	1.28
Example 2	1.03	1.40	1.18
Example 3	0.98	0.94	0.85
Comparative Experiment C	0.98	0.43	0.82
Comparative Experiment D	1.00	1.00	1.00
Comparative Experiment G	1.00	1.00	1.00

Claims

1. A process for preparing highly active hydrotreating catalysts having surface areas above 300 m^2/g and at least about 80% of the pore diameters less than 7 nm, which process comprises:

(a) precipitating an aqueous solution of one or more aluminium salt(s) by adjusting the pH of said solution to a range between 5.5 and 10.0 at a temperature in the range between 20°C and 90°C, thereby forming a precipitate,

(b) ageing the precipitate at a temperature ranging from 20°C to 90°C for at least 15 minutes at a pH ranging from 8.0 to 12.0,

(c) washing the precipitate,

(d) mixing the precipitate with dry, water-soluble salts of a heavy metal selected from the group consisting of molybdenum, tungsten and mixtures thereof and either of cobalt or of nickel and a phosphorus-containing compound in an amount of from 0.2 to 1.5 moles of phosphorus per mole of heavy metal, at a pH in the range between 4.0 and 8.0 and a temperature in the range between 25°C and 100°C to yield a final catalyst having from 1%w to 5%w of cobalt or nickel and from 8%w to 32%w heavy metal,

(e) extruding the product of step (d), and

(f) drying and calcining the product of step (e) at a temperature ranging from 300°C to 900°C.

2. A process according to claim 1, wherein step (a) comprises titrating an aqueous solution of an acid aluminium salt and an aqueous solution of a basic aluminium compound at a pH in the range between 5.5 and 10.0 and a temperature in the range between 20 °C and 90 °C, thereby forming a precipitate.

3. A process according to claim 1, wherein step (d) comprises mixing a dry, water-soluble salt of a heavy metal selected from the group consisting of molybdenum, tungsten and mixtures thereof, and a mixture of a dry, water-soluble cobalt salt and a phosphorus-containing compound or a mixture of a dry, water-soluble nickel salt and a phosphorus-containing compound having an amount of from 0.2 to 1.5 moles of phosphorus per mole of heavy metal with the precipitate at a pH in the range between 4.0 and 8.0 and a temperature in the range between 25 °C and 100 °C to yield a final catalyst having from 1%w to 5%w of cobalt or nickel and from 8%w to 32%w heavy metal.

4. A process according to claim 2, wherein step (d) comprises mixing a dry, water-soluble salt of heavy metal selected from the group consisting of molybdenum, tungsten and mixtures thereof, and a mixture of a dry, water-soluble cobalt salt and a phosphorus-containing compound or a mixture of a dry, water-soluble nickel salt and a phosphorus-containing compound having an amount of from 0.2 to 1.5 moles of phosphorus per mole of heavy metal with the precipitate at a pH in the range between 4.0 and 8.0 and a temperature in the range between 25 °C and 100 °C to yield a final catalyst having from 1%w to 5%w of cobalt or nickel and from 8%w to 32%w heavy metal.

5. A process according to claim 1, wherein step (a) comprises titrating an aqueous solution of an acid aluminium salt selected from the group consisting of aluminium sulphate, aluminium nitrate and aluminium chloride, and an aqueous solution of a basic aluminium compound selected from the group consisting of sodium aluminate and potassium aluminate, at a pH in the range between 5.5 and 8.0 at a temperature in the range between 20 °C and 90 °C, thereby forming a precipitate, and step (d) comprises mixing the precipitate with dry, water-soluble nickel salts and molybdate or dimolybdate salts, and phosphoric acid in an amount of from 0.2 to 1.5 moles of phosphorus per mole of molybdenum or with dry, water-soluble cobalt salts and molybdate or dimolybdate salts and optionally phosphoric acid in an amount of from 0.2 to 1.5 moles of phosphorus per mole of molybdenum, at a pH in the range between 4.0 and 6.0 and a temperature in the range between 25 °C and 100 °C to yield a final catalyst having from 2.5%w to 4%w of cobalt or nickel and from 10%w to 14%w molybdenum.

6. A process according to claim 1, wherein step (a) comprises precipitating an aqueous solution of an acid aluminium salt selected from the group consisting of aluminium sulphate, aluminium nitrate and aluminium chloride, and an aqueous solution of a base at a pH in the range between 5.5 and 8.0 at a temperature in the range between 20 °C and 90 °C, and step (d) comprises mixing the precipitate with dry, water-soluble nickel salts and molybdate or dimolybdate salts and phosphoric acid in an amount of from 0.2 to 1.5 mole of phosphorus per mole of molybdenum or with dry, water-soluble cobalt salts and molybdate or dimolybdate salts and optionally phosphoric acid in an amount of from 0.2 to 1.5 moles of phosphorus per mole of molybdenum at a pH in the range between 4.0 and 6.0 and a temperature in the range between 25 °C and 100 °C to yield a final catalyst having from 2.5%w to 4%w of cobalt or nickel and from 10%w to 14%w molybdenum.

7. A process according to claim 1, wherein step (a) comprises precipitating an aqueous solution of an acid with an aqueous solution of a basic aluminium compound selected from the group consisting of sodium aluminate and potassium aluminate, at a pH in the range between 5.5 and 8.0 at a temperature in the range between 20°C and 90°C, and wherein step (d) comprises mixing the precipitate with dry, water-soluble nickel salts and molybdate or dimolybdate salts, and phosphoric acid in an amount of from 0.2 to 1.5 moles of phosphorus per mole of molybdenum or with dry, water-soluble cobalt salts and molybdate or dimolybdate salts and optionally phosphoric acid in an amount of from 0.2 to 1.5 moles of phosphorus per mole of molybdenum, at a pH in the range between 4.0 and 6.0 and a temperature in the range between 25°C and 100°C to yield a final catalyst having from 2.5%w to 4%w of cobalt or nickel and from 10%w to 14%w molybdenum.

8. A process according to one or more of claims 1-7 wherein step (a) is carried out at a pH in the range between 5.5 and 8.0.

9. A process according to one or more of claims 1-8 wherein step (a) is carried out at a temperature between 50°C and 85°C.

10. A process according to one or more of claims 1-9 wherein step (b) is carried out at a pH in the range between 9.0 and 11.0.

11. A process according to one or more of claims 1-10 wherein step (d) is carried out in such a way as to give a final catalyst having from 2.5%w to 4%w of cobalt or nickel and from 8%w to 18%w molybdenum.

12. A catalyst which comprises a catalytically effective amount of cobalt or nickel and a catalytically effective amount of a heavy metal selected from molybdenum, tungsten and mixtures thereof, on an alumina support, said catalyst having a surface area greater than 300 m^2/g and at least 80% of its pore volume in pores having diameters less than 7 nm, wherein said catalyst has been prepared by a process according to one or more of claims 1-11.

13. A process for hydrotreating hydrocarbon-containing feeds wherein a catalyst is used which has been prepared by a process according to one or more of claims 1-11.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 87 20 2073

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	US-A-4 003 828 (P.E. EBERLY) * Example 1; table 1; claims 7-9 * ---		B 01 J 27/188 B 01 J 21/04 B 01 J 27/16 C 10 G 45/08 B 01 J 37/04
A	US-A-4 560 466 (S.G. KUKES) * Example 4; claims 1-4 * ---		
A	US-A-3 969 273 (S.M. BROWN) * Claim 4 * ---		
A	US-A-3 493 517 (J. JAFFE) ---		
A	US-A-4 066 572 (M.E. CHOCA) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			B 01 J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14-01-1988	THION M.A.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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